



Short communication

## A novel FeAs anode material for lithium ion battery

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ABSTRACT

FeAs powders are prepared using iron and arsenic as the reactants by solid state reaction. The electrochemical performances of FeAs materials as the anode for lithium ion batteries are investigated. The FeAs electrode delivers a reversible lithium-insertion capacity of ca. 817 and 424 mAh g<sup>-1</sup> in the cut-off voltage range of 0.01–2.0 V and 0.3–1.2 V, respectively. The latter range ensures a good cycling stability of FeAs electrode. A possible lithiation/delithiation mechanism is proposed according to the HRTEM observation on cycled electrodes. The results show that FeAs is a potential electrode material for lithium ion batteries. Considering the open layered structure characteristic of some superconductors, which is beneficial to the insertion/extraction of lithium ion, they may be the candidate electrodes for lithium ion batteries.

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### 1. Introduction

Graphite is now widely applied commercially in lithium-ion batteries due to its low cost and excellent cycling performance [1–6]. However, the theoretical capacity of graphite anode material is only 372 mAh g<sup>-1</sup>, corresponding to LiC<sub>6</sub>-GICs (graphite intercalation compounds), and its practical capacity so closely approaches the theoretical value that further improvement is difficult [7–10]. Based on the challenge facing graphite, more and more research on other anode materials for lithium-ion batteries is now being carried out. The search for the alternative anode materials to graphite is indispensable.

Since F-doped LaFeAsO, as a superconductor with the highest T<sub>c</sub> (transition temperature) of ca. 26 K, was first reported in 2008 [11], a broad family of FeAs-based superconductors such as LnFeAsO and BFeAsF for “1111” compounds, BFe<sub>2</sub>As<sub>2</sub> for “122” compounds, AFeAs for “111” compounds, Sr<sub>3</sub>Sc<sub>2</sub>Fe<sub>2</sub>As<sub>2</sub>O<sub>5</sub> for “32225” compounds and Sr<sub>4</sub>M<sub>2</sub>Fe<sub>2</sub>As<sub>2</sub>O<sub>6</sub> for “42226” compounds, where A, B, Ln and M are alkaline, alkaline earth, rare earth and transition metals, respectively, has been discovered (the numerical values correspond to the composition ratio) [12]. The FeAs-based superconductors adopt a quasi-two-dimensional crystal structure, where [Fe<sub>2</sub>As<sub>2</sub>] blocks are separated either by atomic A, B sheets or by [LnO], [BF] blocks or by more complex perovskite-like blocks.

The [FeAs] layer is believed to be crucial to support the superconductivity in iron arsenide superconductors [12–14]. In recent years, new superconductors LiFeAs and NaFeAs have been reported, which are synthesized with Li/Na and FeAs as the reactants by solid-state reaction, and their superconductivities have been intensively investigated [12–17]. FeAs exhibits a possible ability for lithium storage. And it should be pointed out that FeP has showed lithium storage capability as the anode for lithium ion batteries [18–20].

Inspired by the investigations of FeAs-based superconductors, we attempt to investigate the possibility of FeAs used as a novel anode material for lithium ion batteries in this study. The electrochemical behavior of FeAs is examined, and a possible mechanism for the lithiation/delithiation process is proposed. The experimental results confirm that FeAs has great promise as an anode material for lithium ion batteries.

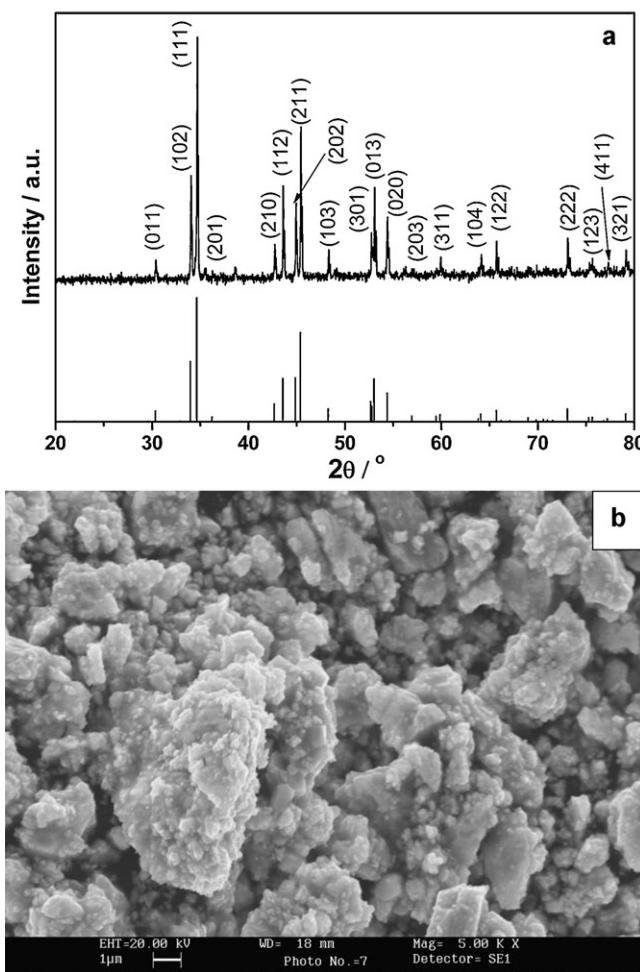
### 2. Experimental

FeAs was prepared using Fe powder and arsenic bulk by solid state reaction. The starting materials were mixed in a mole ratio of 1:1, and then transferred into a quartz tube. After evacuation, the quartz tube was sealed by an oxyhydrogen flame. The tube was then put into a muffle furnace, heated to 800 °C at 5 °C min<sup>-1</sup>, and calcined at 800 °C for 10 h.

X-ray diffraction (XRD) was performed to identify the phase composition of as-prepared FeAs powders over the 2θ range from 20 to 80° using a Rigaku D/max-A diffractometer with Cu Kα radiation. The morphology of as-prepared FeAs powders was observed using a LEO-1450 scanning electron microscope (SEM). The lattice

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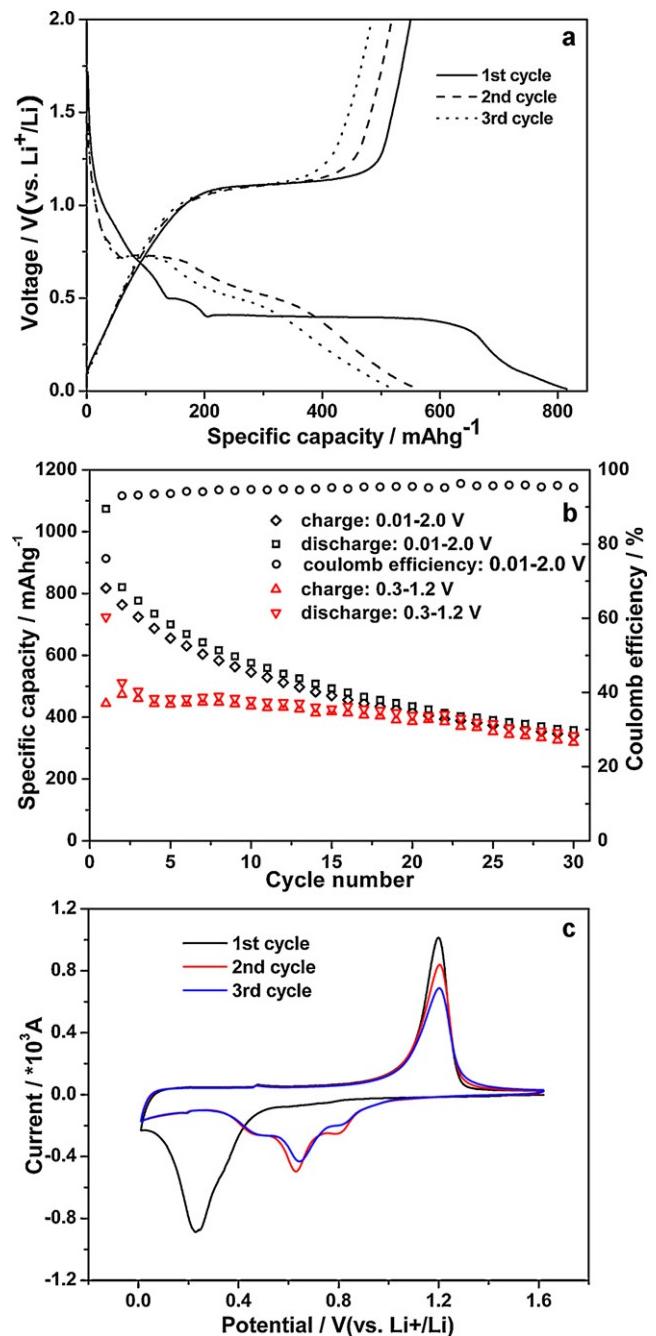
**Fig. 1.** (a) XRD pattern of as-prepared FeAs powders and (b) SEM image of ball-milled FeAs powders.

structure of cycled FeAs material was examined by JEM-2010 and JEM-100CX II high-resolution transmission electron microscope (HRTEM) with selected area electron diffraction (SAED).

The working electrodes were prepared by mixing as-prepared FeAs powders as active material, acetylene black as conductive agent and polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidinone (NMP) as binder in a weight ratio of 70:15:15. After well mixed, the slurry was then coated on the copper foil, used as current collector, by tape-casting method. The electrode film was exposed to air to evaporate NMP and then dried in vacuum at 120 °C for 24 h. The half cells were assembled in an argon-filled glove box using lithium foil as the counter electrode, Celgard 2400 as the separator, the solution of 1 M LiPF<sub>6</sub> in DMC:DEC:EC (1:1:1, WW<sup>-1</sup>) as the electrolyte. The cells were galvanostatically discharged and charged by LAND BT-10 tester (Wuhan, China). Cyclic voltammetry was performed at the scan rate of 0.1 mV s<sup>-1</sup> on a CHI600A electrochemical workstation.

### 3. Results and discussion

The XRD pattern of as-prepared FeAs powders is shown in Fig. 1(a). The standard powder X-ray diffraction data of FeAs (PDF No. 65-0163) is also given for comparison with as-prepared FeAs. All the peak positions and the relative peak intensities of as-prepared FeAs powders are very consistent with those of the standard PDF card of FeAs. No obvious peaks assignable to oxides

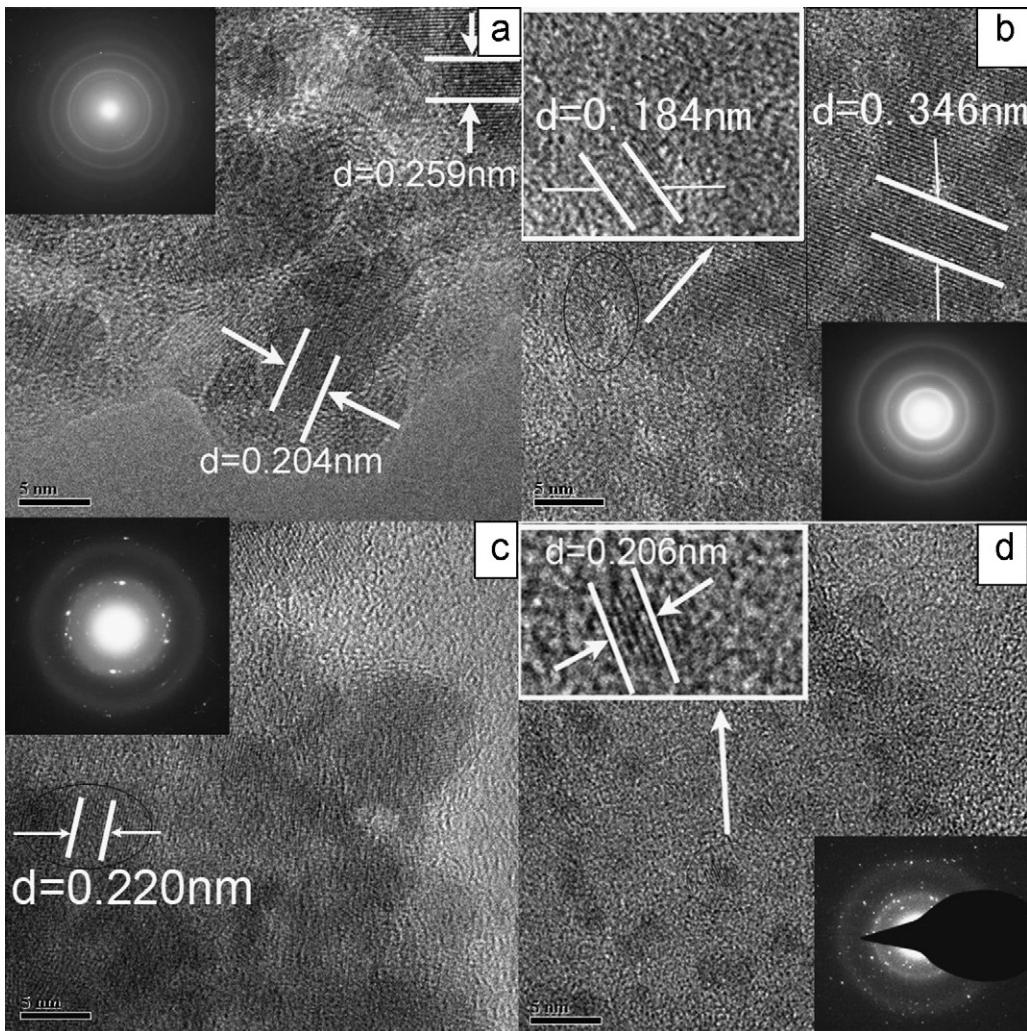


**Fig. 2.** Electrochemical performances of FeAs anode: (a) voltage profiles for the initial three cycles for as-prepared FeAs anode; (b) cycling performance for ball-milled FeAs anode; (c) plots of cyclic voltammetry of as-prepared FeAs anode.

are identified, while some weak peaks are observed at the diffraction angles of 36–40° and 54–58°, which may be assigned to FeAs<sub>2</sub> but it is difficult to confirm this. FeAs has an orthorhombic structure (Pnma) of the MnP-type (B31) with  $a = 5.454 \text{ \AA}$ ,  $b = 3.33 \text{ \AA}$  and  $c = 6.027 \text{ \AA}$  [15,16,21,22].

The as-prepared FeAs powders were milled for 15 min by high-energy ball milling. The SEM image of ball-milled FeAs powders is shown in Fig. 1(b). They exhibit irregular particle morphology, wide particle size distribution and considerable particle aggregation.

The as-prepared FeAs powders were subjected to the charge/discharge test in an FeAs/Li half-cell at a current density of 100 mA g<sup>-1</sup> with the cut-off voltage of 0.01–2.0 V. Fig. 2(a) shows the initial three cycles. It displays an initial discharge capacity



**Fig. 3.** HRTEM images of FeAs anodes (inset: selected area electron diffraction patterns and zoomed images): (a) discharged to 0.4 V; (b and c) discharged to 0.01 V; (d) discharged to 0.01 V and subsequently charged to 3.0 V.

of  $815 \text{ mAh g}^{-1}$  and charge capacity of  $550 \text{ mAh g}^{-1}$  with an initial coulombic efficiency of ca. 67.5%. As a novel anode material, FeAs demonstrates high capacities exceeding that of graphite. The initial irreversible capacity mainly comes from the formation of a solid electrolyte interphase (SEI) film, as indicated by the discharge potential slope in the range of 1.0–0.5 V. In the first cycle, there are two discharge potential plateaus appearing at 0.5–0.4 V and 0.4 V, respectively. From the second cycle onwards, the previous discharge potential plateau disappears, and two discharge potential plateaus appear instead at 0.8–0.7 V and 0.6–0.4 V. The difference in discharge potential between initial and subsequent cycles indicates different lithiation process. Charge voltage profiles at the initial and subsequent charge processes are similar, showing an obvious plateau at ca. 1.1 V.

In order to mitigate the capacity fade, the as-prepared FeAs powders were subjected to high-energy ball milling. Fig. 2(b) illustrates the cycling performance of ball-milled FeAs at  $100 \text{ mA g}^{-1}$  in different cut-off voltage ranges, 0.01–2.0 V and 0.3–1.2 V. When charged/discharged between 0.01 and 2.0 V, the ball-milled FeAs electrode delivers an initial discharge and charge capacity of 1074 and  $817 \text{ mAh g}^{-1}$ , respectively, but exhibits gradual capacity degradation with cycling. After 30 cycles, the discharge and charge capacity remains 358 and  $341 \text{ mAh g}^{-1}$ . The coulombic efficiency is 76.1% at the first cycle and then keeps at ca. 95.3% in the subsequent cycles. When the cut-off voltage is changed to 0.3–1.2 V,

the cycling performance of FeAs electrode is obviously improved, although the initial discharge and charge capacity decreases to 724 and  $444 \text{ mAh g}^{-1}$ , respectively.

Increasing the lower limit of voltage will make Li-insertion insufficient, which leads to less volume expansion of the FeAs anode, while decreasing the upper limit of voltage can reduce the electrode polarization. Both of them are favorable for the good cycling stability of FeAs electrode. It is reported that the loss of electronic contact of active material due to the volume change occurs in the delithiation process in silicon anodes, but not in the lithiation process [23]. Therefore, decreasing the upper limit of voltage may reduce volume shrinkage, maintaining electronic contact, and thus improve the cycle performance.

As a novel anode material, the investigation on the lithiation/delithiation mechanism of FeAs is necessary for better understanding on the electrochemical properties. The structure variation of FeAs electrode after lithiation/delithiation was characterized by XRD. Unfortunately, we did not get any valuable information from XRD patterns (not shown here) due to amorphization of FeAs during lithiation/delithiation process.

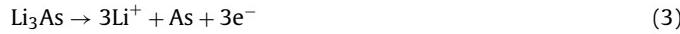
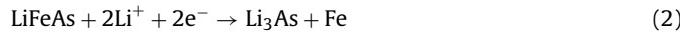
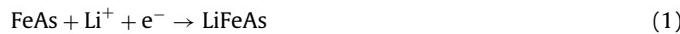
The HRTEM images and the SAED patterns of FeAs electrodes charged/discharged to different voltages are shown in Fig. 3. Small ordered domains are dispersed in a disordered matrix. When an FeAs anode is discharged to 0.4 V, the characteristic distances of ordered domains are 0.259 and 0.204 nm, which are closed to the

interplanar distances of (1 1 0) plane (0.26700 nm), and (1 1 2) plane (0.20434 nm) of LiFeAs (PDF No. 65-4947), respectively. The SAED pattern of the electrode reveals a series of rings. The corresponding interplanar distances are 0.1931, 0.1394, 0.1141 and 0.0896 nm, which can be assigned to (1 1 2), (2 0 3), (1 1 5) and (2 1 6) planes of LiFeAs. When discharged to 0.01 V, the stripe distances change to 0.346, 0.220 and 0.184 nm, closed to the interplanar distances of (1 0 1) plane (0.34235 nm) and (2 0 1) plane (0.18496 nm) of Li<sub>3</sub>As (PDF No. 65-3513), respectively. The set of SAED rings for the sample can be indexed as Li<sub>3</sub>As, which can be assigned to (1 0 1), (1 1 2) and (2 1 4) planes. The characteristic distance of 0.220 nm is closed to the interplanar distance of (1 1 1) plane (0.21099 nm) of Fe (PDF No. 65-9094). The rings for the SAED of the sample can also be mainly indexed to Fe.

When discharged to 0.01 V and subsequently charged to 3.0 V, the characteristic distance is 0.206 nm, which is closed to the interplanar distance of (1 1 0) plane (0.21099 nm) of Fe (PDF No. 65-9094). The interplanar distances of the SAED patterns are 0.211 nm and 0.110 nm, which can be assigned to (1 1 1) and (3 1 1) planes of Fe.

Based on the above analysis, a possible lithiation/delithiation mechanism of FeAs materials is proposed as follows.

In the first cycle:



In the subsequent cycles:



Initially, Li<sup>+</sup> inserts into the crystal lattice of FeAs to form LiFeAs at the potential of 0.5 V. With Li<sup>+</sup> sequentially inserting, the structure of LiFeAs collapses, and LiFeAs transforms into Li<sub>3</sub>As and Fe at ca. 0.4 V. During charging, Li<sup>+</sup> extracts from Li<sub>3</sub>As at 1.1 V, producing arsenic. In the following cycles, Li<sup>+</sup> reversibly inserts into arsenic at 0.8–0.4 V or extracts from Li<sub>3</sub>As at 1.1 V. Fe does not participate in the electrochemical reaction and thus can buffer the volume change of As during cycling, improving the cycling performance. The detailed mechanism needs to be determined by further experiments.

The cyclic voltammetry plots of as-prepared FeAs electrode for the initial three cycles are presented in Fig. 2(c). A cathodic peak at 0.23 V is observed in the first cycle, and disappears in the following cycles, which corresponds to the combination of irreversible reactions (1) and (2). In the second and third discharge cycles, the cathodic peak at 0.6 V occurs instead, corresponding to the reaction (4). All the anodic peaks remain at 1.2 V, which should be attributed to the reversible reaction (5).

#### 4. Conclusion

FeAs powders were prepared from Fe and As by solid state reaction. FeAs as an anode material delivers a reversible capacity of ca. 817 mAh g<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup> with the

cut-off voltage of 0.01–2.0 V. After 30 discharge/charge cycles, the reversible capacity of ca. 341 mAh g<sup>-1</sup> is maintained. Narrowing the cut-off voltage range to 0.3–1.2 V can remarkably improve the cycling stability of FeAs electrode. A possible lithiation/delithiation mechanism of FeAs is proposed according to the HRTEM observation on the cycled electrode. FeAs is a potential electrode material for lithium ion batteries. The investigations show that certain superconductors with open layer structures appear to be effective hosts for the insertion/extraction of lithium ions, and arsenic and metal arsenide may have the Li-storage ability. Of course, the toxic feature of As-based materials will limit their practical application.

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